

VII-B Electronic Structure and Reactivity of Metal Cluster Complexes

Because trimetal cluster complex is a fundamental framework for constructing high nuclearity cluster, electronic structure and reactivity of trimetal cluster complex is important. We have studied the electronic structure and reactivity of bis(μ_3 -benzylidyne)tris(cyclopentadienylcobalt) complex. It reacts halogens and silver(I) to give halide and silver bridged complexes.

VII-B-1 Synthesis, Structure and Redox Behavior of Tricobalt Cluster with Capping Benzylidyne and Bridging halogen $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2(\mu\text{-X})]^+$ ($X = \text{Cl}, \text{Br}, \text{I}$)

EBIHARA, Masahiro; IIBA, Masami¹; MATSUOKA, Hiroaki¹; KAWAMURA, Takashi¹
(¹Gifu Univ.)

Reactions of the benzylidyne capped tricobalt cluster $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2]$ (**1**) with halogens ($X_2 = \text{Cl}_2, \text{Br}_2, \text{I}_2$) in CH_2Cl_2 gave oxidative addition products of halogen to **1**. X-ray structures of four salts, $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2(\mu\text{-Cl})]\text{PF}_6 \cdot \text{CH}_3\text{CN}$ ($2^+\text{PF}_6^- \cdot \text{CH}_3\text{CN}$), $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2(\mu\text{-Br})]\text{SbF}_6$ (3^+SbF_6^-), $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2(\mu\text{-I})]\text{SbF}_6 \cdot \text{CH}_2\text{Cl}_2$ ($4^+\text{SbF}_6^- \cdot \text{CH}_2\text{Cl}_2$) and $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2(\mu\text{-I})]\text{I}_3$ (4^+I_3^-) were determined. In all structures the halogen atom was in the Co_3 plane. The halogen-bridged Co–Co distance was elongated ($2^+\text{PF}_6^- \cdot \text{CH}_3\text{CN}$: 2.6072(5) Å, 3^+SbF_6^- : 2.6097(9) Å, $4^+\text{SbF}_6^- \cdot \text{CH}_2\text{Cl}_2$: 2.621(2) Å) and the Co–Co distances without halogen-bridge remained unchanged (2^+PF_6^- : 2.4038(9) and 2.3947(7) Å, 3^+SbF_6^- : 2.3902(8) and 2.4015(9) Å, $4^+\text{SbF}_6^- \cdot \text{CH}_2\text{Cl}_2$: 2.392(2) and 2.388(2) Å) from that of **1** (2.38 Å). Cyclic voltammogram of 2^+PF_6^- in CH_2Cl_2 with 0.1 M *n*-Bu₄NPF₆ as supporting electrolyte showed a quasi-reversible oxidation (+0.75 V, potential vs Fc/Fc⁺) and an irreversible reduction wave (−0.57 V) (Figure 1). The irreversible reduction caused recovery of neutral cluster complex **1**. The redox properties of **3**⁺ and **4**⁺ were similar to that of **2**⁺. Cyclic voltammetry of **1** in 0.1 M *n*-Bu₄NCl/CH₃CN with various scan rates indicated that the formation of **2**⁺ was a multi-step reaction. First **1** was oxidized to **1**⁺ and it was coordinated by Cl[−] and immediately oxidized to **2**⁺.

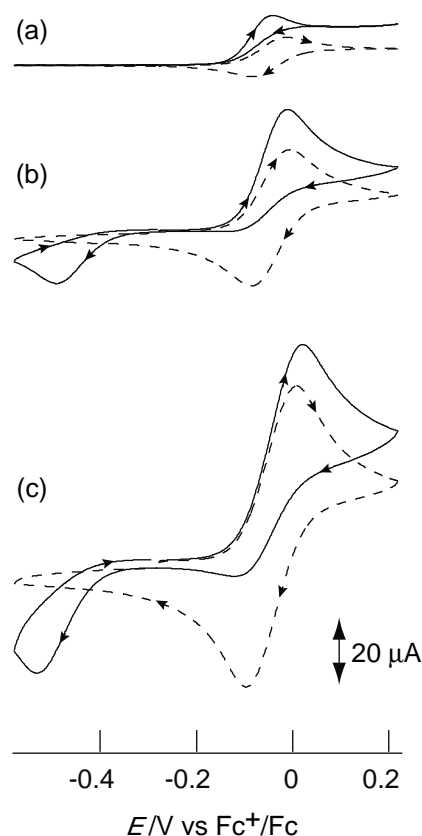


Figure 1. Cyclic voltammograms of **1** (2.0 mM) in CH_3CN with 0.1 M *n*-Bu₄NCl. Scan rate (a) 10 mVs^{−1}, (b) 100 mVs^{−1} and (c) 500 mVs^{−1} with cyclic voltammograms of **1** (2.0 mM) in 0.1 M *n*-Bu₄NPF₆ (broken line).

VII-B-2 Bis- μ_3 -Benzylidyne Tri(cyclopentadienylcobalt) Cluster with Edge-bridging Silver(I): Synthesis, Structure and Solution Properties of $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2\{\mu\text{-Ag(X)}\}]$ ($X = \text{CF}_3\text{CO}_2, \text{NO}_3$) and $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2\{\mu\text{-Ag}(\text{NCCH}_3)\}]\text{PF}_6$

EBIHARA, Masahiro; IIBA, Masami¹; MATSUOKA, Hiroaki¹; KAWAMURA, Takashi¹
(¹Gifu Univ.)

Reactions of the benzylidyne capped tricobalt cluster $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2]$ (**1**) with various silver salts are examined. The salts of weakly- or non-coordinating anions (BF_4^- , PF_6^-) oxidize **1** to its cationic radical $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2]^+$ (**1**⁺) in CH_2Cl_2 . The reaction with the salts of strongly-coordinating anions (CF_3CO_2^- , NO_3^-) gives silver(I) adducts of **1**, $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2\{\mu\text{-Ag(X)}\}]$ ($X = \text{CF}_3\text{CO}_2^-$ (**2**, Figure 1), NO_3^- (**3**)). Even for AgBF_4 or AgPF_6 the reaction in CH_3CN produces silver(I) adduct $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2\{\mu\text{-Ag}(\text{NC-}$

$\text{CH}_3\}}\text{]}^+$ (4^+). The Co_3Ag skeleton in structures of **2**, **3** and 4^+ resembles each other. The Co–Co bonds bridged by the Ag atom (**2**: 2.4783(9) Å, **3**: 2.481(1) Å, 4^+ : 2.4600(9) Å) are longer than that of **1** (2.38 Å). The other Co–Co bonds are slightly shorter than that in **1**. The Co_2Ag triangle is not coplanar with the Co_3 triangle; the dihedral angles between these triangles for **2**, **3**, and 4^+ are 162.7°, 157.8°, and 151.3°, respectively. Dissolution of 4^+PF_6^- in CH_2Cl_2 causes formation of 1^+ with deposition of Ag metal. ^1H NMR spectra of **2** and **3** in CD_2Cl_2 indicates partial dissociation of the AgX group. The ^1H NMR spectra of CD_3CN solutions and the ESR spectra in frozen CH_3CN solutions of **2**, **3**, and 4^+PF_6^- shows generation of 1^+ without deposition of Ag metal. It suggests that equilibrium of Ag^+ and **1** with Ag^0 and 1^+ is established in acetonitrile. Addition of AgO_2CCF_3 to the solution causes disappearance of the ESR signal. It indicates that 1^+ is generated from 4^+ or the reaction of **1** with anion-uncoordinated Ag^+ .

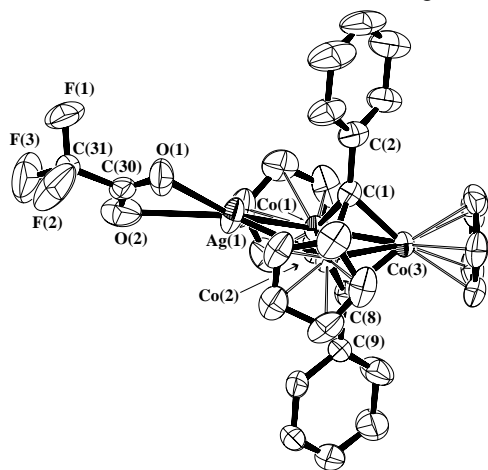


Figure 1. Structure of $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2\{\mu\text{-Ag}(\text{O}_2\text{CCF}_3)\}]$.